

CHEMICAL COMMINUTION OF COAL

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ABSTRACT

Chemical comminution is an effective means for size reduction and beneficiation of coal. Sodium hydroxide and i-propanol show synergism in chemical comminution of Illinois No. 6 bituminous coal.

The system was effective at low alkali concentrations with low consumption of NaOH. Much of the NaOH consumed was for neutralization of acidity of the coal. Isopropanol serves only as a reaction medium and could be recovered nearly quantitatively for recycle. The system lends itself to application in preparation of coal-water mixture and coal-alcohol slurry fuels.

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INTRODUCTION

The use of coal as a source of energy and hydrocarbons will become more important in the future. In the upgrading and utilization of coal, size reduction is an important preparative step. The beneficiation of coal needs extensive crushing and the preparation of coal-water fuel mixtures, requires even finer particle size. Size reduction by mechanical means is not only energy intensive but also causes heavy wear on the processing equipment.

An alternative method of coal comminution is to weaken the coal structure by chemical action. This concept has been applied to remove mineral matter from coal (1), to desulfurize coal (2,4,5) and to facilitate in-situ coal extraction from underground deposits (6).

Various reagents which have been studied for chemical comminution include pure and aqueous ammonia, alkals such as NaOH, KOH, Na_2CO_3 , $\text{Ca}(\text{OH})_2$, etc. and organic solvents (3,7). The common limitations of the above-mentioned approaches are high reagent consumption and a low degree of effectiveness.

Among the systems studied, NaOH in high concentration (>0.1 N) is one of the most promising. However, the NaOH consumption is >5 wt% of treated coal and this makes it unattractive for practical applications.

We discovered that NaOH and i-propanol show synergism in coal comminution and that coal can be effectively comminuted by NaOH at concentrations less than 0.1 N in 90% i-propanol/water, with a low alkali consumption. The alcohol is not consumed chemically in the process and can be recovered quantitatively for reuse. The mechanism and kinetics of coal-alkali reactions were also investigated.

EXPERIMENTAL

Coal Sample: Illinois No. 6 Bituminous Coal, with the size in the range of 1-1.2 cm³ were hand-picked for the experiments.

Comminution Solution: Reagent grade NaOH and i-propanol were used as received. The comminution solution was prepared as a 9 to 1 volume ratio of i-propanol to aqueous NaOH stock solution. The different NaOH concentrations of the comminution solution were obtained by varying the concentration of NaOH stock solutions. The normality of the NaOH solution is calculated based on the total volume of the caustic and iso-PROH.

Coal Comminution Procedure: Seventy-five ml of comminution solution and 10 g of coal were reacted in a sealed stainless steel vessel at 100°C for 48-86 hours. The treated coal was recovered by filtration and dried in a 100°C oven overnight.

The effect of chemical comminution was judged by the following standards:

- o Very extensive: Coal sample is disintegrated into 10 or more smaller pieces.
- o Extensive: Coal sample is disintegrated into less than 10 pieces of smaller coal.
- o Good: Little coal is degraded. Coal has well developed cracks all over the surface and samples can be crumbled with hand pressure.
- o Fair: Little or no smaller coal pieces are found. Cracks on coal surface are formed mainly along the seam.

The pH values of the initial and spent solution were analyzed with a pH meter. The NaOH concentration of the corresponding solutions were determined by titration.

Determination of i-propanol Consumption: A thick-walled Pyrex tube divided into two compartments with a medium porous glass frit in the middle was employed. Comminution solution (50 ml) was first introduced into the tube and allowed to drain through the frit and fill the lower compartment. Coal (60-100 mesh, 10 g) was then charged into the upper compartment. After the tube was sealed, the tube was inverted to allow the comminution solution to contact the coal. The sealed tube was heated at 100°C at this position for 48 hrs.

After the heating period, the sealed tube was inverted back to its original position to disengage liquid and solid. The coal was dried by freezing the liquid compartment in liquid N_2 and heating the coal compartment with wrapped heating tape. The coal and the solution were recovered by opening the sealed tube and their weights were determined. The i-propanol content in the solution was determined by gas chromatography. A series of experiments consisting of three repeats averaged 99% material balance and i-propanol consumption was 0.1-0.7%.

Determination of NaOH Consumption Rate: A Brinkmann autotitrator E526 was used. Coal (0.5 g, 200+ mesh) was suspended in 50 ml of 90% i-propanol aqueous solution under an argon atmosphere and titrated against 0.01 N NaOH at a pH of 7.

Determination of the Neutralization Equivalent of Coal: Aliquots of 1 ml, 0.5 N NaOH were added to 5 g of coal (200 mesh) suspended in 50 ml of 90% i-PROH. The pH change was followed by a pH meter. Additional NaOH was added when the pH dropped below 7. This procedure was repeated until a steady pH of 7 was reached.

RESULTS AND DISCUSSION

Synergism of NaOH and Alcohols: Alcohol by itself is a very weak comminution agent. Storing coal under alcohols such as methanol, ethanol and i-PrOH for an extended period of time does not weaken the coal structure. Similarly, sodium hydroxide at concentrations lower than 0.1 N is not an effective comminution agent.

It is found in this study that by combining those two ineffective agents, an efficient comminution solution was obtained. Thus, dilute NaOH at levels of 0.025-0.1 N in 90% i-propanol is very effective for comminuting coal with low alkali consumption. Without i-propanol, the concentration of NaOH at these levels is too low to comminute the coal. In the presence of i-propanol, extensive comminution is achieved with low alkali consumption. To achieve these levels of comminution without i-propanol, the NaOH consumption would have been 6.2 wt% of treated coal for 0.1 N NaOH solution. In the presence of isopropanol the typical levels of alkali consumption are in the range of 0.7-2.0 wt% of treated coal (Table 1). For example, the NaOH consumption for an extensive comminution is 2.6% for 0.1 N NaOH in 90% i-PrOH.

The much enhanced comminution effect of NaOH-i-PrOH relative to aqueous NaOH is due to several possible causes:

1. As polar organic compounds, alcohols wet coal better than water and facilitate the contact between alkali and coal. The observed trend in terms of effective comminution medium is:



Apparently higher alcohols are better comminution solvents due to their higher affinity to and more effective wetting of the coal surfaces.

2. The reactivity of the OH^- anion may be enhanced by the solvation of Na^+ cations by alcohol molecules relative to aqueous solution so that the OH^- becomes more exposed and free to attack acidic substrates. It is well known that crown ethers, THF, polyalkylene polyamines are capable of "trapping" alkali and alkali earth cations (13). Therefore n-butyl lithium is a much stronger nucleophile in THF, crown ethers and tetramethylenediamine than in hexane.

Effect of Alkali Concentration: The initial alkali concentration was varied between 0.01 and 0.1 N. Notwithstanding the 10-fold increase in NaOH concentration, the initial pH of the comminution solution remained constant at about 12.5 (Table 1). It is suspected that the 90% i-propanol solution is saturated with NaOH at a concentration greater than 0.01 N. At NaOH concentrations greater than 0.01 N, the solutions appeared turbid.

A linear relationship exists between the initial NaOH concentration and consumption of alkali (Figure 1). The alkali consumption can be lowered by using a more dilute alkali solution but its effectiveness for comminution is reduced. The lowest NaOH concentration in 90% i-PrOH sufficient to comminute coal is about 0.028 N. The NaOH consumption in this case is 0.7 wt% of the coal. This alkali concentration probably is the most cost effective for coal comminution.

At higher NaOH concentrations, the consumption of NaOH increases as the comminution becomes more extensive. At 0.1 N NaOH concentration the degradation of coal structure was extensive and the alkali consumption reached 2.6%. This condition probably is the upper limit for economical coal comminution. (The criteria of comminution effect are defined in the experimental section.)

To obtain effective coal comminution, a minimum pH of 10 should be maintained. It is clear that run A4 and B4 (Table 1) had inadequate alkali strength to result in poor comminution. The alkali concentrations used in A3 and B3 are optimum for good comminution effects.

Alkali Consumption: The alkali consumed in the chemical comminution in the presence of i-PrOH is mainly for neutralization of acidity (8) in the coal. Phenols (9) and carboxylic acids constitute the bulk of the acids in coal. Other materials which consume alkali are metal oxides and minerals. A pH value of 3.4 was detected for a coal/water suspension (0.5 g

of 200 mesh + coal in 50 ml H_2O) indicating the acidic nature of coal.

Alkali consumption due to the acidity in the coal was obtained by neutralizing it exhaustively using dilute NaOH at pH 7. It took 1.4 wt% of NaOH based on coal to neutralize the coal. Since this value is very close to those runs in which extensive comminution was obtained (A2 and B2), we are tempted to conclude that much of the NaOH consumption is for neutralization of acidity in the coal.

Iso-propanol Consumption: The role of alcohol in the comminution of coal using a NaOH - i-PrOH - H_2O system is probably as a solvent which enhances NaOH reactivity rather than as a chemical reagent. By employing a sealed tube technique described in the experimental section, 99.2-99.9% of i-PrOH was recovered from the spent solution. This extremely high i-PrOH recovery rate supports that it does not react with coal functionalities. The very high recovery of alcohol could make the comminution method described in this paper viable for industrial applications.

Kinetics of NaOH Uptake: As mentioned above, much of the alkali taken up by coal is for neutralization of the acid sites of the coal. Therefore, a fast reaction between alkali and coal is expected. The uptake of alkali by coal in an iso-propanol - H_2O system at a constant pH of 7 and 25°C was studied using an automatic titrator. To simplify the analysis of kinetic data the OH^- concentration was kept constant.

Plotting the log of NaOH uptake rate against the log of the reaction time, a straight line with a slope of -0.5 was obtained (Figure 3). Thus, the rate of caustic uptake can be represented with the following equation.

$$r = 2.33 \times 10^7 t^{-0.5}$$

where r is the rate of caustic uptake, mole/sec. Kg of coal,
 t is time, sec.

The form of this equation suggests that the reaction is rapid and the reaction rate is mass transfer limited. The initial rate at reaction time of 0.01 sec is in the range of 10^8 mole/sec. Kg which is too fast for organic reactions likely to occur in this system at room temperature. A rate of 10^{-4} to 10^{-6} mole/sec. is expected for typical organic reactions. On the other hand, the reaction rate of H^+ and OH^- is mass transfer limited at a rate of 10^{10} mole/sec. (11). For the neutralization of weak acids in coal it is expected to be somewhat slower than that for the strong acids. A rate of 10^8 mole/sec. Kg is reasonable. This supports the assumption that neutralization of acids in coal is the major reaction in the comminution of coal.

The mechanism of the above reaction can be modeled with the reaction controlled by diffusion through the "ash" layer of a shrinking core. According to this model, and following the notation used by Levenspiel (10),
 the rate of reaction $-\frac{dN}{dt}$

at any time can be expressed by

$$\frac{-dN}{dt} \left(\frac{1}{r_c} - \frac{1}{R} \right) = 4 \pi D_e C \quad (1)$$

$$t = \frac{\rho R^2}{6D_e C} \left[1 - 3 \left(\frac{r_c}{R} \right)^2 + 2 \left(\frac{r_c}{R} \right)^3 \right] \quad (2)$$

where N is conc. of reacting OH⁻ ion, mole

r_c , R are the radii of the reacting core at t and the original particle, respectively, cm

D_e is the effective diffusivity, cm²/sec

C is the concentration of OH⁻ ions in the bulk phase mole/cc

ρ is density of coal, g/cc

For complete conversion of a particle, the time required is

$$T = \frac{\rho R^2}{6D_e C} \quad (3)$$

The dimensionless time $\left(\frac{t}{T} \right)$ is

$$\frac{t}{T} = 1 - \left(\frac{r_c}{R} \right)^2 + 2 \left(\frac{r_c}{R} \right)^3 \quad (4)$$

$$\frac{t}{T} = 1 - 3(1-X)^{2/3} + 2(1-X) \quad (5)$$

where X is conversion, fraction.

According to Equation 5, conversion, and in turn NaOH consumption rate was calculated as a function of time using a computer. By plotting the log of NaOH consumption rate, $\log dN/dt$ against $\log t$, a straight line with a slope of -0.53 was obtained (Figure 2). A similar plot using experimental data also yielded a straight line with a slope of -0.5 (Figure 3). The excellent agreement between the experimental and calculated values demonstrate the validity of this model. Examination of the model indicates that this linear relationship is valid up to a conversion level of about 80%.

The D_e can be estimated from the experimental data. Since the real time for $x = 0.5$ and $t/T = 0.11$ was 5400 sec., the time for complete conversion T was calculated to be 49,090 sec. according to Equation (5). The effective diffusivity D_e calculated from Equation (3) is 1×10^{-6} cm²/sec. This magnitude of diffusivity compares reasonably with literature values, e.g., the self-diffusion rates of Br^- in 1 and 6% cross-linked divinyl benzene (Dowex 2 anion resin) at 25°C are 9 and 4×10^{-7} cm²/sec, respectively (12). The consistent value of D_e obtained further substantiates the validity of the model.

SUMMARY

Chemical comminution is an effective method for size reduction and beneficiation of coal. Although NaOH is effective at a concentration >0.1 N, the alkali consumption can be as high as 5-10 wt % of coal treated which makes it unattractive for practical applications.

We find that there is a synergistic comminution effect when NaOH is used in combination with alcohols. Such a system is more effective than NaOH or alcohols when used separately.

This synergistic effect of NaOH/alcohol may be due to its higher affinity for coal and better penetrating ability than that of NaOH/H₂O. A higher alcohol (i-propanol) was found to be more effective than methanol probably due to its larger organic groups. Another contributing factor to the synergism might be the solvation of Na^+ by alcohol which renders the OH^- more

exposed and therefore, a more reactive species. Alcohol appears not to be involved in coal-NaOH reactions, since it can be recovered almost quantitatively. Its role in comminution is a reaction medium to facilitate the OH^- /coal contact.

There is a linear relationship between initial NaOH concentration and its consumption. A higher degree of comminution was affected at higher NaOH consumption. A 0.028 N of NaOH in 90% i-PrOH was effective in coal comminution with an NaOH consumption of only 0.73% of coal. The NaOH consumption is mainly for neutralizing the acidity of the coal. The NaOH consumption for neutralization and exhaustive coal comminution were essentially the same. Studies of NaOH uptake by coal at a fixed pH of 7 using an autotitrator showed that the diffusion of alkali into coal is the rate controlling step in NaOH-coal reaction.

Coal comminution with NaOH-alcohols is effective and could find applications in coal-water slurry and coal-alcohol slurry preparations.

REFERENCES

1. P. H. Howard and R. S. Datta, "Chemical Comminution: A Process for Liberating the Mineral Matter from Coal," Symposium on Desulfurization of Coal and Coal Char," Amer. Chem. Soc. National Meeting, New Orleans, March 20-25, 1977.
2. R. G. Aldrich, "Chemical Comminution of Coal and Removal of Ash Including Sulfur in Inorganic Form Therefrom," U.S. Patents 3,870,237 (1975), 3,918,761(1975).
3. J. N. Chew and J. G. Savins, private communication.
4. P. H. Howard, A. Hanchett and R. G. Aldrich, "Chemical Comminution for Cleaning Bituminous Coal," Clean Fuels from Coal Symposium II, Institute of Gas Technology, June 23-27, 1975, Chicago, Illinois.
5. C. Y. Tai, G. V. Graves and T. D. Wheelock, "Desulfurization of Coal by Oxidation in Alkaline Solutions," Third Symposium on Coal Preparation, NCA/BCR Coal Conference and Expo IV, Oct. 1977, Louisville, KY.
6. R. G. Aldrich, D. V. Keller, Jr. and R. G. Sawyer, "Chemical Comminution and Mining of Coal," U.S. Patent 3,815,826, (1974).
7. I. G. C. Dryden, "Solvent Power for Coals at Room Temperature," Chem. Indust., 502, June 1952.
8. P. K. Dutta and R. J. Holland, Fuel 62 732 (1983).
9. M. Farcasiu, Fuel 56 9 (1977).
10. O. Levenspiel, "Chemical Reaction Engineering," p. 364-367, 2nd Ed., John Wiley and Sons, Inc., New York, 1972.
11. R. P. Bell, "Acids and Bases," p. 65, Chapter 6, 2nd Ed., Methnen and Co. Ltd., London, 1969.
12. B. A. Soldano and G. E. Boyd, "Self-diffusion of Anions in Strong Base Anion Exchangers," J. Amer. Chem. Soc., 75, 6099 (1953).
13. C. J. Pedersen, Aldrichimica. Acta, 4, 1 (1971).

Figure 1. NaOH Consumption - Initial NaOH Concentration

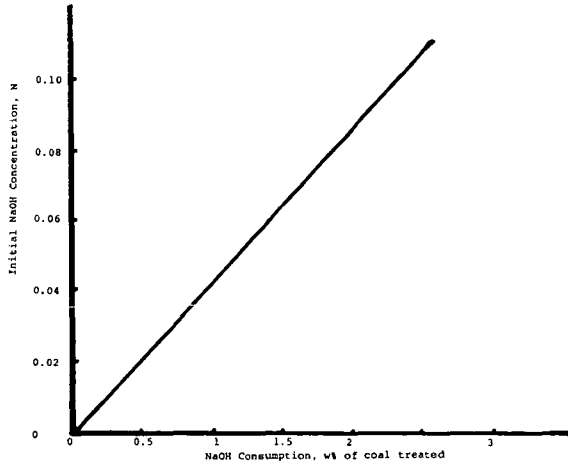
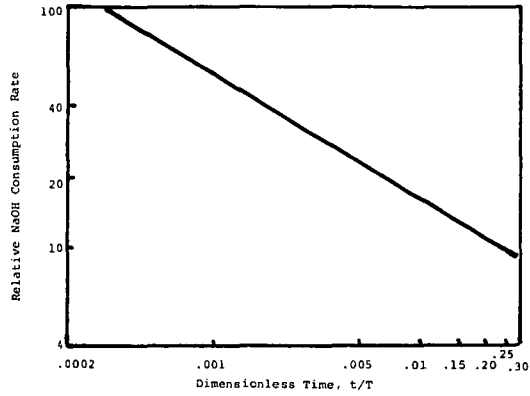


Figure 2. Predicted NaOH Consumption Rate



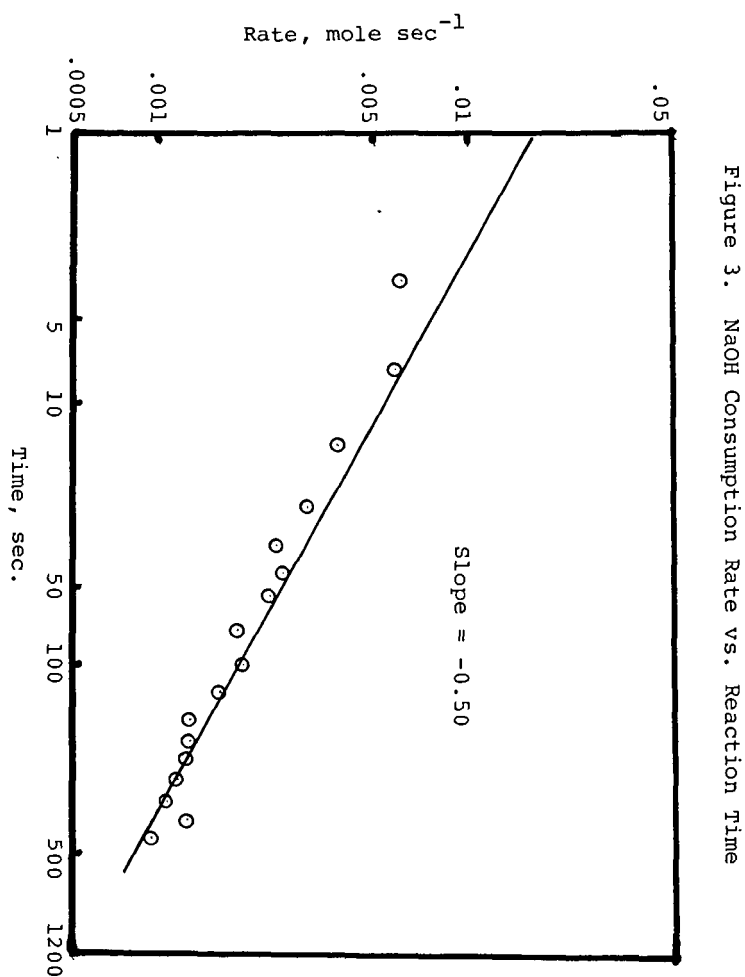


Table 1

Comminution of Illinois No. 6 Bituminous Coal
with NaOH in 90% i-Propanol

Experiment	NaOH Conc. N	Solution pH		NaOH Consumption wt% of coal	Results**	
		Initial	Final			
A*	1	0.111	12.49	11.94	2.59	Very extensive
	2	0.0456	12.49	11.94	1.2	Extensive
	3	0.028	12.48	10.62	0.73	Good
	4	0.011	12.50	8.85	0.28	Fair
B**	1	0.099	12.58	11.93	2.62	Very extensive
	2	0.0452	12.49	11.09	1.20	Extensive
	3	0.0282	12.47	10.72	0.75	Good
	4	0.0104	12.52	8.8	0.25	Fair

* 48 hr @ 100°C, 1/4-1/2 in³ coal used

** 96 hr @ 100°C, 1 in³ coal used.